

Guided Exercises for Quantum Chemistry



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The current source for these materials is accessible on Github:
<https://github.com/jlaaser/quantum-exercises>

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Quantum States: Analogies to Functions and Vectors

Quantum states are abstract, but we can get some intuition for their properties by drawing *analogies* to functions and vectors.

1. Use your knowledge about functions and vectors to predict what expression should go in each of the blank cells in this table. A few of the lines are filled out to get you started.

Functions	Vectors	Quantum States
$f(x)$	$\vec{v} = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}$	$ \alpha\rangle$
$f^*(x)$	$\vec{v}^\dagger = \begin{pmatrix} v_1^* & v_2^* & v_3^* \end{pmatrix}$	$\langle\alpha $
$h(x) = f(x) + g(x)$	$\vec{w} = \vec{u} + \vec{v}$	$ \gamma\rangle = \alpha\rangle + \beta\rangle$
	$(c\vec{v})^\dagger = c^* \vec{v}^\dagger$	
$\int_{-\infty}^{\infty} dx f^*(x)f(x)$	$\vec{v}^\dagger \vec{v}$	$\langle\alpha \alpha\rangle$
	$(\vec{u}^\dagger \vec{v})^* = \vec{v}^\dagger \vec{u}$	
$\int_{-\infty}^{\infty} dx f^*(x)f(x) \geq 0$		
		$\langle\beta c \alpha\rangle = c \langle\beta \alpha\rangle$

Note: we are using a very general notation here that allows vectors and functions to have complex values. If \vec{u} and \vec{v} are purely real, however, then $\vec{u}^\dagger \vec{v}$ is just equal to the dot product $\vec{u} \cdot \vec{v}$ - I encourage you to try working through this if you are unsure about why it should be true.

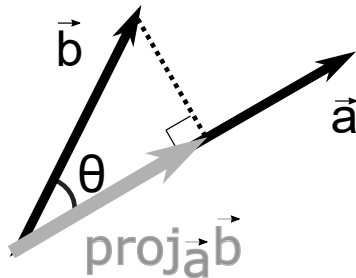
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2. If \vec{a} is a vector, then $\vec{a}^\dagger \vec{a}$ gives the square of the length of the vector.

(a) Why is it always true that $\vec{a}^\dagger \vec{a} > 0$?

(b) In this context, how would you interpret $\langle \alpha | \alpha \rangle$?

3. If \vec{a} and \vec{b} are vectors, then the *projection* of \vec{b} onto \vec{a} is



$$\begin{aligned}
 \text{proj}_{\vec{a}} \vec{b} &= (\text{length}) (\text{direction}) \\
 &= (|\vec{b}| \cos(\theta)) \left(\frac{\vec{a}}{|\vec{a}|} \right) \\
 &= \left(|\vec{b}| \frac{\vec{a}^\dagger \vec{b}}{|\vec{a}| |\vec{b}|} \right) \left(\frac{\vec{a}}{|\vec{a}|} \right) \\
 &= \frac{\vec{a}^\dagger \vec{b}}{|\vec{a}|^2} \vec{a}
 \end{aligned}$$

In this context, how would you interpret the following expression?

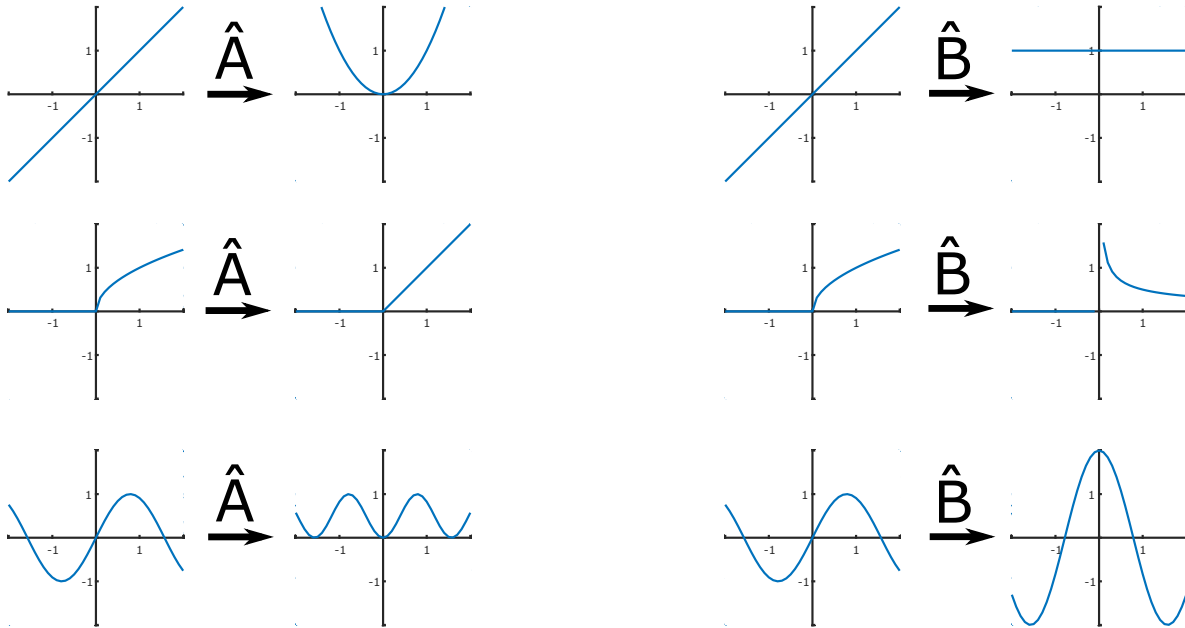
$$\frac{\langle \alpha | \beta \rangle}{\langle \alpha | \alpha \rangle} |\alpha\rangle$$

STOP HERE.

Understanding Operators

In this exercise, you will again use functions as a model for understanding some of the properties of operators. (You will do a similar exercise with vectors on your first problem set.)

1. \hat{A} and \hat{B} are operators that each operate on a function (left column) to give a new function (right column).



(a) Describe, in words, what each operator does to a function.

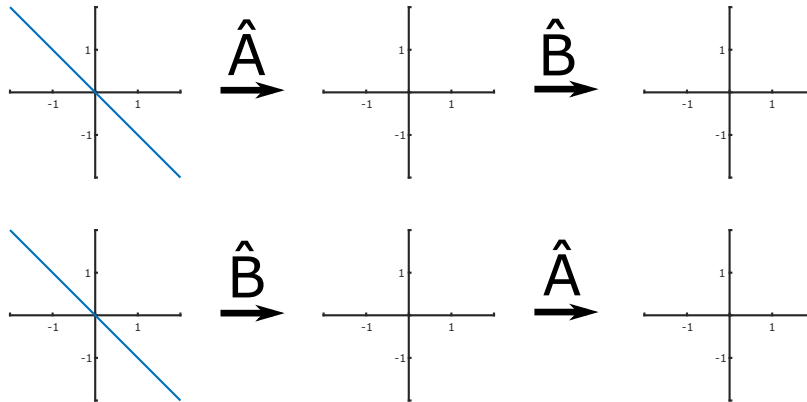
(b) Fill in the blanks by writing mathematical forms for each operator:

$$\hat{A}f(x) = \boxed{}$$

$$\hat{B}f(x) = \boxed{}$$

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- (c) Predict what functions would result from the following operations:



If the function on the left is $f(x)$, then one of the plots on the right corresponds to $\hat{A}\hat{B}f(x)$ and one corresponds to $\hat{B}\hat{A}f(x)$. Circle the plot that you think corresponds to $\hat{A}\hat{B}f(x)$.

- (d) From your results, do you think $\hat{A}\hat{B}|\Psi\rangle$ will usually be equal to $\hat{B}\hat{A}|\Psi\rangle$? Why or why not?

- (e) Are there any functions $f(x)$ and $g(x)$ for which $\hat{A}f(x) = f(x)$ and $\hat{B}g(x) = g(x)$? If so, what are they?

STOP HERE.

Eigenfunctions and Eigenvalues

1. Assume $|f\rangle$ is an eigenket of $\hat{\Omega}$ with eigenvalue ω , i.e.

$$\hat{\Omega}|f\rangle = \omega|f\rangle$$

- (a) What is $\langle f|\hat{\Omega}|f\rangle$? You may assume $|f\rangle$ is normalized.

- (b) What is $\langle f|\hat{\Omega}|f\rangle^*$?

- (c) If $\hat{\Omega}$ is Hermitian, then your answers to the preceding two parts have to be equal. What does that tell you about the values of ω and ω^* ?

- (d) If a number is equal to its complex conjugate, then can the number have a non-zero imaginary part? Why or why not?

- (e) What does that tell you about the value of ω ?

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2. The Kronecker delta, δ_{ij} , equals 1 when $i = j$ and is 0 when $i \neq j$.

(a) Write out the first few terms of the sum $\sum_j \delta_{3j} c_j$. What does it simplify to?

(b) More generally, what do you think $\sum_j \delta_{ij} c_j$ will simplify to?

3. We can always choose the eigenstates $\{|i\rangle\}$ of a Hermitian operator such that the overlap of an eigenstate with itself equals 1 and the overlap of an eigenstate with a different eigenstate equals 0, i.e. such that

$$\langle i | j \rangle = \delta_{ij}$$

(a) If we write $|\Psi\rangle$ as a linear combination of these eigenstates, i.e.

$$|\Psi\rangle = \sum_j c_j |j\rangle$$

what is $\langle i | \Psi \rangle$?

(b) Substitute your answer back into $|\Psi\rangle = \sum_j c_j |j\rangle$.

Why might we say that $\sum_i |i\rangle \langle i|$ is just equivalent to multiplying by 1?

STOP HERE.

Wavefunctions and Probabilities

If $|\Psi\rangle = \sum_i c_i |i\rangle$, where the $\{|i\rangle\}$ are the eigenstates of operator $\hat{\Omega}$, then

$$\begin{aligned}\langle\Psi|\hat{\Omega}|\Psi\rangle &= \left(\sum_i c_i^* \langle i|\right) \hat{\Omega} \left(\sum_j c_j |j\rangle\right) \\ &= \sum_i |c_i|^2 \omega_i\end{aligned}$$

(You will prove this on your first homework set.)

1. This has a similar form to a weighted average, e.g.

$$\langle\omega\rangle = \sum_i P_i \omega_i$$

where P_i is the probability of measuring value ω_i . In this context, how would you interpret $|c_i|^2$?

2. Remember that you can find c_i by calculating $\langle i|\Psi\rangle$. Given this, how would you interpret the value of $|\langle i|\Psi\rangle|^2$?

3. A particularly useful set of eigenstates are the eigenstates of the position operator, \hat{x} , where eigenstate $|x_1\rangle$ corresponds to the eigenstate in which we measure the position of the particle as being exactly at $x = x_1$ and nowhere else.

In this context, how would you interpret the value of $|\langle x_1|\Psi\rangle|^2$?

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4. More generally, how would you interpret the function $|\Psi(x)|^2$ where $\Psi(x) = \langle x|\Psi\rangle$?

5. What should have to be true about the value of $\int_{-\infty}^{\infty} dx |\Psi(x)|^2$?

Hint: what should the total probability of finding the particle somewhere along the x axis be?

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Time-Evolution of the Wavefunction

We can describe the time-evolution of a quantum state $|\Psi\rangle$ using the time-evolution operator $\hat{U}(t)$, which relates the state of the system at time $t = t_1$ to the state of the system at time $t = 0$ by

$$|\Psi(t = t_1)\rangle = \hat{U}(t_1) |\Psi(t = 0)\rangle$$

$\hat{U}(t)$ is given by

$$\hat{U}(t) = e^{-i\hat{H}t/\hbar}$$

where \hat{H} is the Hamiltonian operator corresponding to the total energy of the system.

1. If $|n\rangle$ is an eigenstate of \hat{H} , then

$$\hat{H} |n\rangle = E_n |n\rangle$$

where E_n is the total energy of a system in eigenstate $|n\rangle$.

Using this information, fill in the blanks for the following expressions:

$$\hat{H}^2 |n\rangle = \hat{H} (\hat{H} |n\rangle) = \boxed{} \quad \hat{H}^3 |n\rangle = \boxed{} \quad \hat{H}^i |n\rangle = \boxed{}$$

2. Applying $\hat{U}(t)$ directly to $|n\rangle$ is tricky because \hat{H} is in the exponent. However, we can do it if we use the Taylor-series expansion $e^x \approx 1 + x + \frac{1}{2!}x^2 + \dots$

Fill in the blanks in the following derivation:

$$\begin{aligned} \hat{U}(t) |n\rangle &= e^{-i\hat{H}t/\hbar} |n\rangle \\ &= \left(1 + \boxed{} + \frac{1}{2!} \boxed{} + \dots \right) |n\rangle \\ &= \left(|n\rangle + \left(\frac{-it}{\hbar} \right) \hat{H} \boxed{} |n\rangle + \frac{1}{2!} \left(\frac{-it}{\hbar} \right)^2 \hat{H} \boxed{} |n\rangle + \dots \right) \\ &= \left(|n\rangle + \left(\frac{-it}{\hbar} \right) E_n \boxed{} |n\rangle + \frac{1}{2!} \left(\frac{-it}{\hbar} \right)^2 E_n \boxed{} |n\rangle + \dots \right) \\ &= \left(1 + \boxed{} + \frac{1}{2!} \boxed{} + \dots \right) |n\rangle \\ &= e^{-iE_n t/\hbar} |n\rangle \end{aligned}$$

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3. If we express $|\Psi(t=0)\rangle$ as a linear combination of energy eigenstates, e.g.

$$|\Psi(t=0)\rangle = \sum_n c_n |n\rangle$$

then how would you find $|\Psi(t=t_1)\rangle$?

(Hint: start by substituting this expression into $|\Psi(t=t_1)\rangle = \hat{U}(t_1) |\Psi(t=0)\rangle$, and note that you can move $\hat{U}(t_1)$ through the sum since it is a linear operator.)

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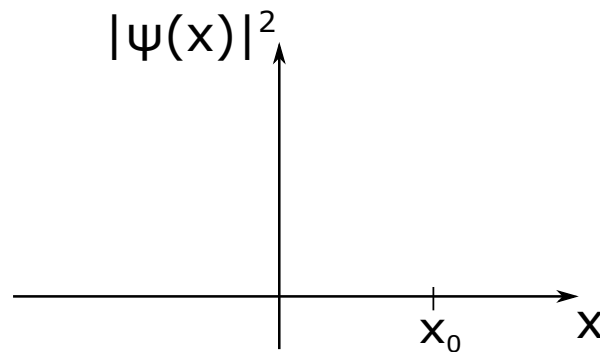
Position and Momentum: Eigenfunctions and Operators

Two particularly useful operators in quantum mechanics are the position operator, \hat{x} , and the momentum operator, \hat{p} .

In this set of exercises, we will consider what these operators and their eigenfunctions look like in the position representation.

1. An eigenstate of the position operator is one where the probability of finding the particle is nonzero at only one position.

(a) Predict what the probability density for a particle found at $x = x_0$ should look like:



- (b) The eigenvalue of this position eigenstate should be the particle's position, e.g. x_0 . Which of the following operators would be most useful for extracting this eigenvalue?

$$\hat{\Omega}\psi(x) = \psi(x) + x$$

$$(\hat{\Omega} = \text{"add } x\text{"})$$

$$\hat{\Omega}\psi(x) = x\psi(x)$$

$$(\hat{\Omega} = \text{"multiply by } x\text{"})$$

$$\hat{\Omega}\psi(x) = |\psi(x)|^2$$

$$(\hat{\Omega} = \text{"square the function"})$$

$$\hat{\Omega}\psi(x) = \frac{d}{dx}\psi(x)$$

$$(\hat{\Omega} = \text{"take the derivative"})$$

Briefly explain your choice:

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2. De Broglie told us that a particle with momentum p has wavelength $\lambda = \frac{h}{p}$.
- (a) One useful function that has a wave-like form is $f(x) = e^{ikx} = \cos(kx) + i \sin(kx)$. What is the wavelength of this function in terms of k (i.e. for what value of λ does $f(x+\lambda) = f(x)$)?
- (b) Set this wavelength equal to de Broglie's value for λ . How is k related to p ?
- (c) What operator might you be able to apply to the function e^{ikx} to extract the momentum eigenvalue p ?

STOP HERE.

2. (a) It is physically impossible for the particle to be in the regions where $V(x) = \infty$, so the probability of finding the particle in these regions has to be zero.

What does this tell you about the value of the wavefunction in Regions I and III?

$$\Psi_I(x) = \boxed{}$$

$$\Psi_{III}(x) = \boxed{}$$

- (b) The wavefunction must be continuous at every value of x . What does that mean must be true about the value of $\Psi_{II}(x)$ at the edges of the box?

$$\Psi_{II}(0) = \boxed{}$$

$$\Psi_{II}(L) = \boxed{}$$

- (c) Using the wavefunction $\Psi_{II}(x) = A \cos(kx) + B \sin(kx)$, calculate $\Psi_{II}(0)$ and set it equal to the value you found above. What does this tell you about the value of A ?

- (d) Now, calculate $\Psi_{II}(L)$. What has to be true about kL in order for $\Psi_{II}(L)$ to equal what you found in part (b)? What does this result tell you about the values of the energy E ?

STOP HERE.

The Free Particle

Suppose a particle is traveling in a constant one-dimensional potential, $V(x) = V_c$.

1. What is the Hamiltonian for this particle?

$$\hat{H} = \boxed{\phantom{\hspace{10em}}}$$

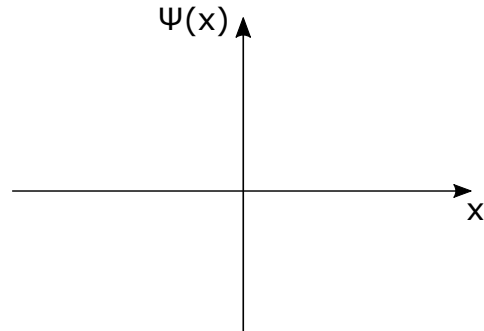
2. What is the Schrödinger equation for this particle?

$$\boxed{\phantom{\hspace{10em}}} = E\Psi(x)$$

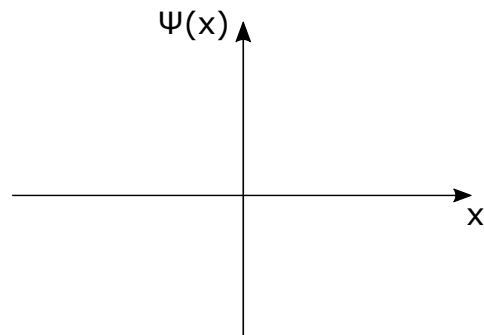
3. Try a solution of the form $\Psi(x) = e^{sx}$. What is s in terms of the potential V_c , the particle's energy E , and the particle's mass, m ?

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4. If the particle's energy is greater than the potential, e.g. $E > V_c$, is s real or imaginary? Sketch the shape of the resulting wavefunction (or wavefunctions) on the graph below:



5. If the particle's energy is less than the potential, e.g. $E < V_c$, is s real or imaginary? Sketch the shape of the resulting wavefunction (or wavefunctions) on the graph below:

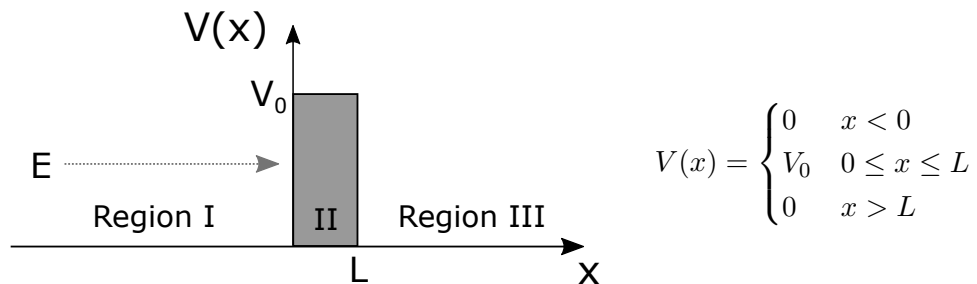


6. Why are the wavefunctions you found in questions 4 and 5 difficult to normalize?

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Tunneling

Consider a particle incident “from the left” on the following potential barrier, with the particle’s energy less than the barrier height, e.g. $0 < E < V_0$:



- What are the general solutions for the wavefunction in each region? Make sure to include any appropriate coefficients and substitute in the correct value of V in each region.

$$\Psi_I(x) = \boxed{\phantom{\Psi_I(x) = A e^{ikx} + B e^{-ikx}}}$$

$$k = \boxed{\phantom{k = \sqrt{2mE}}}$$

$$\Psi_{II}(x) = \boxed{\phantom{\Psi_{II}(x) = C e^{\kappa x} + D e^{-\kappa x}}}$$

$$\kappa = \boxed{\phantom{\kappa = \sqrt{2m(V_0 - E)}}}$$

$$\Psi_{III}(x) = \boxed{\phantom{\Psi_{III}(x) = F e^{ikx}}}$$

- What are the boundary conditions necessary for...

(a) ... the *wavefunction* to be continuous at $x = 0$ and $x = L$?

(b) ... the *first derivative* of the wavefunction to be continuous at $x = 0$ and $x = L$?

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(c) ... the particle to be incident only from the left?

3. What ratio would you calculate if you wanted to find the probability that the particle is transmitted through the barrier (e.g. the tunneling probability)?

4. If you do all the algebra, you will find that the tunneling probability for a tall, thin barrier is approximately

$$T = \frac{16E(V_0 - E)}{V_0^2} e^{-2\sqrt{\frac{2m(V_0 - E)}{\hbar^2}}L}$$

What do you predict would happen to the tunneling probability if...

(a) ... you increased the particle's mass?

(b) ... you decreased the barrier width?

STOP HERE.

Wavepackets

1. Activity time! Get everyone in your group to stand up and stand shoulder-to-shoulder in a straight line. You may go out in the hallway if you need more room.

- (a) Have everyone walk forward for 5 seconds. Try to walk at as close to the same speed as possible. Mark each person's initial and final positions on the following axis:

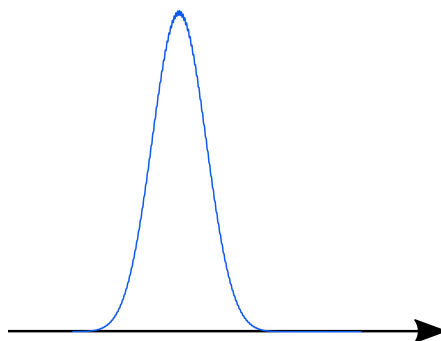


- (b) Go back to your starting line. Have everyone walk forward for 5 seconds again, but this time, designate at least one person as a “fast” walker and one as a “slow” walker. Mark each person's initial and final positions on the following axis:



- (c) In which of these two “simulations” was the uncertainty in your momentum higher? How was it reflected in your final position distribution?

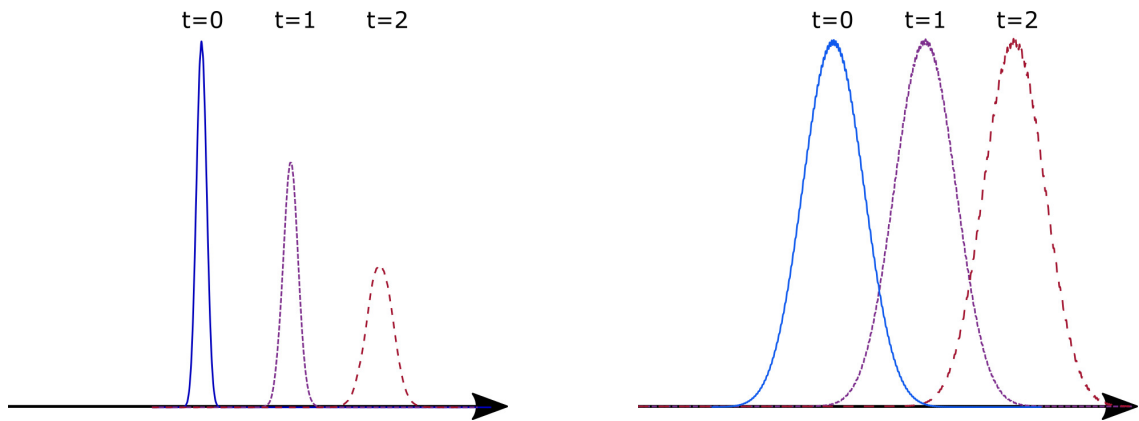
2. Consider a Gaussian wavepacket traveling to the right. At $t = 0$, its probability distribution might look like this:



- (a) Based on the simulation you just did, what feature of this plot (if any) do you think gives you information about the uncertainty in the particle's position? Mark it on the plot.
- (b) Similarly, what feature of this plot (if any) gives you information about the uncertainty in the particle's momentum? Mark it on the plot.

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3. The following plots show the propagation of two different wavepackets:



(a) Which wavepacket has the larger uncertainty in the position, and which has the larger uncertainty in the momentum?

(b) Explain how your observations relate to the uncertainty principle.

STOP HERE.

Generalizing the Free Particle

In this set of exercises, we will explore how to think about an arbitrary wavefunction on a constant potential in terms of the free particle momentum eigenstates.

1. Let's start by considering how the wavefunction in the position representation is related to the wavefunction in the momentum representation.

(a) The wavefunction in the position representation is given by $\Psi(x) = \langle x | \Psi \rangle$.

Insert a complete set of momentum eigenstates at the arrow and simplify to find an expression for $\Psi(x)$ in terms of $\Psi(k)$.

(b) Use the same process to find an expression for $\Psi(k) = \langle k | \Psi \rangle$ in terms of $\Psi(x)$.

(c) Do you notice anything interesting about these relationships? If you know the formal name for this type of transformation, go ahead and write it down:

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2. Now, let's consider the time-dependence of a particle on a constant potential.

- (a) If a system starts in a pure momentum eigenstate, i.e. $\Psi(x, t = 0) = \phi_k(x)$, what is its *time-dependent* wavefunction $\Psi(x, t)$?

You'll probably find it useful to remember that on a constant potential $V(x) = 0$, the momentum eigenstate with quantum number k has wavefunction $\phi_k(x) = e^{ikx}$ and energy $E_k = \frac{\hbar^2 k^2}{2m}$.

- (b) For a discrete set of eigenstates, a particle with $\Psi(x, t = 0) = \sum_n c_n \phi_n(x)$ has time-dependent wavefunction $\Psi(x, t) = \sum_n c_n e^{-iE_n t/\hbar} \phi_n(x)$.

By analogy, what do you think the time-dependent wavefunction should be for a particle with $\Psi(x, t = 0) = \int_{-\infty}^{\infty} dk c(k) \phi_k(x)$?

STOP HERE.

A Few Special Operators

In this set of exercises, we will look at the raising and lowering operators and their effect on eigenstates of the harmonic oscillator.

1. We showed that we can write the dimensionless Hamiltonian for the harmonic oscillator as

$$\hat{h} = \hat{a}^\dagger \hat{a} + \frac{1}{2}$$

This is just an operator ($\hat{N} = \hat{a}^\dagger \hat{a}$) plus a constant ($c = \frac{1}{2}$).

- (a) Suppose $|n\rangle$ is an eigenstate of \hat{N} with eigenvalue n , i.e. $\hat{N}|n\rangle = n|n\rangle$. Is $|n\rangle$ also an eigenstate of \hat{h} ?

- (b) How are the eigenvalues of $|n\rangle$ under \hat{N} and \hat{h} related?

- (c) Why does this mean we can solve the harmonic oscillator simply by finding the eigenstates of $\hat{a}^\dagger \hat{a}$?

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2. Now, let's consider what eigenvalue we would get from \hat{N} if our starting state were $\hat{a}|n\rangle$. We can write

$$\begin{aligned}
 \hat{N}(\hat{a}|n\rangle) &= (\hat{a}^\dagger \hat{a})\hat{a}|n\rangle && \text{use definition of } \hat{N} \\
 &= (\hat{a}\hat{a}^\dagger - 1)\hat{a}|n\rangle && \text{use } [\hat{a}, \hat{a}^\dagger] = 1 \\
 &= (\hat{a}\hat{a}^\dagger \hat{a} - \hat{a})|n\rangle && \text{distribute} \\
 &= \hat{a}(\hat{a}^\dagger \hat{a} - 1)|n\rangle && \text{"reverse" distribute} \\
 &= \hat{a}(\hat{N} - 1)|n\rangle && \text{use definition of } \hat{N} \\
 &= \hat{a}(n - 1)|n\rangle && \text{use } \hat{N}|n\rangle = n|n\rangle \\
 &= (n - 1)(\hat{a}|n\rangle)
 \end{aligned}$$

- (a) Explain why this means $\hat{a}|n\rangle$ is also an eigenstate of \hat{N} . What is its eigenvalue?

- (b) Explain why this might let us write $\hat{a}|n\rangle = c_n|n - 1\rangle$.

- (c) Why might we call \hat{a} a "lowering" operator?

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3. Now, we need to find the coefficient c_n .

(a) If $|n\rangle$ is normalized, then what is $\langle n|\hat{N}|n\rangle$?

(b) $\langle n|\hat{N}|n\rangle$ can also be written as $\langle n|\hat{a}^\dagger\hat{a}|n\rangle$.

If $\hat{a}|n\rangle = c_n|n-1\rangle$, then $\langle n|\hat{a}^\dagger = c_n^*\langle n-1|$. Using this fact, and remembering that $\hat{N} = \hat{a}^\dagger\hat{a}$, calculate $\langle n|\hat{N}|n\rangle$ in terms of c_n .

(c) Set your answers to the preceding two parts equal to each other. Solve for c_n , and fill in the blank in the following expression:

$$\hat{a}|n\rangle = \boxed{}|n-1\rangle$$

STOP HERE.

Eigenvalues and Eigenstates of the Harmonic Oscillator

1. Let's start by considering the range of values that n can take.
 - (a) We know that for a quantum state α , $\langle \alpha | \alpha \rangle \geq 0$. What does this tell you about the minimum possible value of $\langle n | \hat{a}^\dagger \hat{a} | n \rangle$?
(Hint: start by defining $|\alpha\rangle = \hat{a} |n\rangle$. What is $\langle \alpha |$, and what do you get if you put these pieces together?)
 - (b) We also showed on the previous page that $\langle n | \hat{a}^\dagger \hat{a} | n \rangle = n$. What does this tell you about the minimum possible value of n ?
 - (c) What happens if you try to calculate $\hat{a} |0.5\rangle$? What do you think that means about whether $|0.5\rangle$ is an allowable quantum state for the harmonic oscillator?

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- (d) What happens if you calculate $\hat{a}|1.5\rangle$? Given your answer to part (c), what do you think this means about whether $|1.5\rangle$ is an allowable quantum state?
- (e) Explain why this reasoning suggests that integers are the only allowable quantum numbers for the harmonic oscillator.
2. Suppose we knew what the eigenstate $|0\rangle$ was. What might you do to find eigenstate $|1\rangle$? How about $|2\rangle$, or $|3\rangle$? How about $|n\rangle$?

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Describing States and Operators with Matrices

In this set of exercises, we will look at how vectors and matrices can be used to describe and calculate useful properties of quantum states and operators.

1. (a) Calculate the following matrix product:

$$\begin{bmatrix} c_1^* & c_2^* \end{bmatrix} \begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

- (b) Calculate $\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle$ where $|\psi\rangle = c_1 |1\rangle + c_2 |2\rangle$

- (c) Given your answers to the previous two questions, why might we call $\langle n | \hat{A} | m \rangle$ a “matrix element” of \hat{A} ?

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2. (a) If we calculate matrix elements of \hat{A} using one basis set (e.g. the particle-in-a-box eigenstates), will they be the same as if we use a different basis set (e.g. the harmonic oscillator eigenstates)? Why or why not?
- (b) Determine whether or not the following statement is correct, and briefly explain why or why not: “If $|\Psi\rangle = \sum_n c_n |n\rangle$, and we clearly state what basis states the $\{|n\rangle\}$ represent, then the only thing we need to fully describe $|\Psi\rangle$ are the coefficients c_n .”
- (c) Write an analogous statement about how we might be able to describe \hat{A} solely in terms of its matrix elements.

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Eigenvalues, Eigenstates, and Eigenvectors

In this set of exercises, we will think about how to express eigenvalue-eigenstate relationships using the matrix formalism.

1. (a) Using matrix notation, what needs to be true if $|\Psi\rangle = \sum_n c_n |n\rangle$ is an eigenstate of $\hat{\Omega}$ with eigenvalue ω ?

Hint: in Dirac notation, $|\Psi\rangle$ is an eigenstate of $\hat{\Omega}$ if $\hat{\Omega}|\Psi\rangle = \omega|\Psi\rangle$. What analogous expression do you get if you simply replace $|\Psi\rangle$ and $\hat{\Omega}$ by their matrix-notation equivalents?

- (b) Using your answer to the preceding question, fill in the blank to complete the following statement:

“If $|\Psi\rangle$ is an eigenstate of $\hat{\Omega}$, then the vector $\underline{c} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix}$ must be an of the matrix $\underline{\Omega}$.”

- (c) Suppose we had a matrix $\underline{\Omega}$ containing the matrix elements of $\hat{\Omega}$ in some basis $\{|n\rangle\}$. What steps could you take to find the eigenstates of $\hat{\Omega}$ in terms of the $\{|n\rangle\}$ basis?

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2. Often, it is useful to be able to “transform” the matrix corresponding to an operator (most often the Hamiltonian) from one basis set to another.

(a) Suppose the $\{|n\rangle\}$ are the true eigenstates of \hat{H} , such that $\hat{H}|n\rangle = E_n|n\rangle$. Using Dirac notation, what are the matrix elements of \hat{H} in this basis, i.e. what is H_{nm} ?

(b) Now, assume we only know the matrix elements of \hat{H} in some other basis, $\{|i\rangle\}$. What are the matrix elements in this basis (i.e. what is H_{ij})?

(c) If we take our expression from part (a) and insert a complete set of $\{|i\rangle\}$ eigenstates at each “|”, we get

$$H_{nm} = \sum_i \sum_j \langle n|i\rangle \langle i|\hat{H}|j\rangle \langle j|m\rangle$$

How would you interpret the $\langle n|i\rangle$ and $\langle j|m\rangle$ terms?

(d) If we compiled all of the $\langle n|i\rangle$ values in a matrix $\underline{\underline{S}}$ with matrix elements $S_{ni} = \langle n|i\rangle$, what matrix expression could you use to calculate $\underline{\underline{H}}_{\{|n\rangle\}}$ (the Hamiltonian in terms of the $\{|n\rangle\}$ eigenstates) from $\underline{\underline{H}}_{\{|i\rangle\}}$ (the Hamiltonian in terms of the $\{|i\rangle\}$ states)?

STOP HERE.

Some Properties of the Angular Momentum Operators

In this set of exercises, we will look at commutation relationships of the angular momentum operators. For this set of exercises, you'll find it useful to remember that the operator forms of L_x , L_y , and L_z are given by

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \qquad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \qquad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

1. If we calculate the commutator between \hat{L}_x and \hat{L}_y , we find

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= [\hat{y}\hat{p}_z, \hat{z}\hat{p}_x] - [\hat{y}\hat{p}_z, \hat{x}\hat{p}_z] - [\hat{z}\hat{p}_y, \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \hat{x}\hat{p}_z] \end{aligned}$$

- (a) Two of the commutators in the last line go to zero. Which ones are they, and why are they zero?
- (b) The remaining two commutators simplify to $-i\hbar\hat{y}\hat{p}_x$ and $i\hbar\hat{x}\hat{p}_y$. Which one is which? Can you justify why they have these values?
- (c) Combine your answers to the previous two parts to find an expression for $[\hat{L}_x, \hat{L}_y]$. Your result will be proportional to either \hat{L}_x , \hat{L}_y , or \hat{L}_z - which one is it, and what is the proportionality constant?

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We can generalize the results from the previous page to yield

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z \qquad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x \qquad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

2. (a) Can we measure two different components of the angular momentum simultaneously or not?

- (b) The *square magnitude* of the angular momentum is given by $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$. Do \hat{L}^2 and \hat{L}_z commute?

You'll find it useful to remember that $[\hat{A}^2, \hat{B}] = \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}$

- (c) Based on your result from part (b), can we measure the magnitude of the angular momentum and at least one of its components simultaneously or not?

STOP HERE.

Angular Momentum Raising and Lowering Operators

As with the harmonic oscillator, we can define raising and lowering operators for angular momentum, i.e.

$$\hat{M}_+ = \hat{M}_x + i\hat{M}_y$$

$$\hat{M}_- = \hat{M}_x - i\hat{M}_y$$

1. Let's start by considering whether or not these raising and lowering operators commute with the other angular momentum operators:

(a) What are $[\hat{M}^2, \hat{M}_+]$ and $[\hat{M}^2, \hat{M}_-]$?

(b) What are $[\hat{M}_z, \hat{M}_+]$ and $[\hat{M}_z, \hat{M}_-]$?

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2. Now, let's do what we did for the harmonic oscillator, and assume there exists a state $|Y_{c,b}\rangle$ which is an eigenstate of both \hat{M}^2 and \hat{M}_z , such that

$$\hat{M}^2 |Y_{c,b}\rangle = c |Y_{c,b}\rangle$$

$$\hat{M}_z |Y_{c,b}\rangle = b |Y_{c,b}\rangle$$

- (a) Is $\hat{M}_+ |Y_{c,b}\rangle$ an eigenstate of \hat{M}_z ? If so, what is its eigenvalue?

- (b) Is $\hat{M}_+ |Y_{c,b}\rangle$ an eigenstate of \hat{M}^2 ? If so, what is its eigenvalue?

- (c) Given these results, why might we call \hat{M}_+ a “raising operator” for angular momentum?

STOP HERE.

Eigenvalues of the Angular Momentum Operators

Now that we know something about what the raising and lowering operators do, let's see if we can use them to learn about the allowed eigenvalues for angular momentum.

1. If we apply the raising operator to $|Y_{c,b}\rangle$, we increase the eigenvalue under \hat{M}_z by \hbar , i.e. $\hat{M}_z \hat{M}_+ |Y_{c,b}\rangle = (b + \hbar) \hat{M}_+ |Y_{c,b}\rangle$

- (a) What happens to the eigenvalue under \hat{M}_z if we repeatedly apply \hat{M}_+ (i.e. what is $\hat{M}_z \hat{M}_+^k |Y_{c,b}\rangle$)?

- (b) We know that $\hat{M}^2 = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2$. Can the eigenvalue of \hat{M}_z^2 ever be larger than the eigenvalue of \hat{M}^2 ?

- (c) Using your answer to part (b), fill in the boxes, below, with appropriate inequality symbols (e.g. =, >, <, ≥, ≤, etc.):

$$c \boxed{} b^2$$

or

$$-c^{1/2} \boxed{} b \boxed{} c^{1/2}$$

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2. Our results from the previous page tell us that there are a maximum and minimum allowed value for b . Let's assume the maximum allowed value of b is b_{max} , associated with state $|Y_{c,b_{max}}\rangle$, and the minimum allowed value is b_{min} , associated with state $|Y_{c,b_{min}}\rangle$.

(a) Is $\hat{M}_+ |Y_{c,b_{max}}\rangle$ an allowed state? Why or why not?

(b) We can show that $b_{max} = -b_{min}$. If there are n steps in between, i.e. $b_{max} = b_{min} + n\hbar$, what is b_{max} in terms of n ?

(c) If $j = \frac{n}{2}$, what values can j have?

(d) We can also show that $c = b_{max}^2 + \hbar b_{max}$. What must c be, in terms of j ?

STOP HERE.

The Schrödinger Equation for the Hydrogen Atom

In this set of exercises, we will look at the Schrödinger equation for the Hydrogen-like atom.

1. A “hydrogen-like” atom consists of a nucleus of charge $+Ze$ and mass m_n and an electron of charge $-e$ and mass m_e .

- (a) If the nucleus is at coordinates $\vec{R}_n = (x_n, y_n, z_n)$ and the electron is at $\vec{R}_e = (x_e, y_e, z_e)$, what is the total kinetic energy operator for this system?

Hint: you can simplify the notation by remembering that $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. You can give ∇^2 a subscript to indicate which set of coordinates (nuclear or electronic) it is operating on.

- (b) If the potential energy is given by $V(x_n, y_n, z_n, x_e, y_e, z_e)$, what is the Schrödinger equation for this system?

- (c) We can simplify the potential energy term because the potential is purely electrostatic, and depends only on the *distance* r between the nucleus and the electron, not their absolute positions.

If the electrostatic potential energy for charges Q_1 and Q_2 separated by distance r is $\frac{Q_1 Q_2}{4\pi\epsilon_0 r}$, what is $V(r)$ for the hydrogen-like atom (*hint: what values should you put in for Q_1 and Q_2*)?

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2. If we switch to center-of-mass coordinates, we can separate out the translational motion of the atom from the relative motion of the electron and nucleus.

(a) The *relative* Hamiltonian for the hydrogen-like atom is given by

$$\hat{H}_{rel} = \frac{-\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

Try applying this Hamiltonian to $\Psi(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi)$. How can you simplify this equation? *Hint: remember that $\hat{L}^2 Y_l^m(\theta, \phi) = l(l+1)\hbar^2 Y_l^m(\theta, \phi)$.*

(b) How many quantum numbers should we need to describe the entire spatial wavefunction?

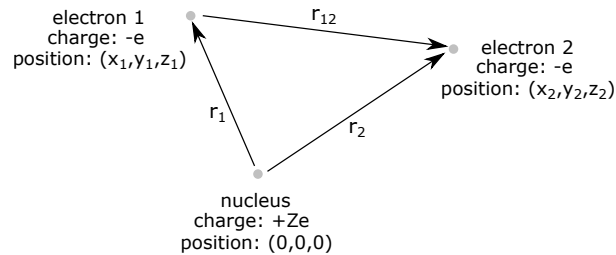
Hint: We know from our discussion of the spherical harmonics that we will need two quantum numbers to describe the angular part of the wavefunction (l and m). How many more do you think you will get from solving the radial part?

(c) Will the radial wavefunctions depend on l ? m ? How about the energies - which quantum numbers do you think they will depend on?

STOP HERE.

The Helium Atom

1. The “helium-like” atom, diagrammed below, is just like a “hydrogen-like” atom, but has two electrons rather than one:



- (a) Assuming the nucleus is fixed in place (i.e. can't move), what is the *kinetic* energy for the helium-like atom? (You may use the ∇^2 notation for the Laplacian(s); just put appropriate subscript(s) on it to indicate which set(s) of coordinates it refers to.)
- (b) What is the *potential* energy for this system? Remember that the electrostatic energy of interaction between particles of charge Q_1 and Q_2 separated by distance r is $\frac{Q_1 Q_2}{4\pi\epsilon_0 r}$.
- (c) What is the *Hamiltonian* for this system?

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- (d) The Hamiltonian you wrote (or should have written!) in part (c) is not separable. Why? Which term causes the problem?
- (e) If you could ignore the “problem” term, what form do you think the wavefunction would take? You may write your answer out in words if you’d like; we’ll formalize the notation together as a class.
- (f) If you calculated an expectation value for the energy using this simplified wavefunction and the full Hamiltonian, do you think the answer would over- or under-estimate the true ground-state energy? Why?

STOP HERE.

The Variational Principle

In this set of exercises, we'll consider the expectation value of the energy for an arbitrary state, $|\Psi_{trial}\rangle$. For these exercises, assume that the $\{|n\rangle\}$ are energy eigenstates, with $\hat{H}|n\rangle = E_n|n\rangle$.

1. Suppose we pick $|\Psi_{trial}\rangle$ such that $|\Psi_{trial}\rangle = \sum_n c_n |n\rangle$.

(a) What is the expectation value of the energy, E_{trial} , for this state?

(b) Assuming that $E_0 < E_1 < E_2 < \dots$ (e.g. the energies increase as n increases), what must be true about the relationship between E_{trial} and E_0 ? Fill in the correct inequality symbol (e.g. $=$, $>$, \geq , $<$, \leq) to express your answer mathematically.

$$E_{trial} \quad \boxed{} \quad E_0$$

(c) If we knew that $|\Psi_{trial}\rangle$ were *orthogonal* to $|0\rangle$, what would have to be true about c_0 ? What energy is the lower bound on E_{trial} in this case?

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2. With the relationships from the previous page in mind, we can revisit the helium atom.
- (a) Suppose we took the same wavefunction that we guessed earlier, but now treat the charge on the nucleus as a *variable* rather than a constant - let's call it Z' rather than Z .

Propose a procedure that you could use to find the value of Z' that gives the “best” possible solution for the ground state energy of the helium atom.

- (b) Do you think the optimized value of Z' will be greater than or less than the “true” value of Z ? Why?

(You should think about this question in purely chemical terms - no math or quantum needed here. Hint: what phenomenon do we talk about when we describe e.g. why some protons have greater chemical shifts in NMR than others?)

STOP HERE.

Symmetry with Respect to Exchange

1. The permutation operator, \hat{P}_{12} , swaps particles 1 and 2, e.g. $\hat{P}_{12}\psi(q_1, q_2) = \psi(q_2, q_1)$.
 - (a) If we apply the permutation operator twice, what should we get? In other words, what is $\hat{P}_{12}^2\psi(q_1, q_2)$?
 - (b) If particles 1 and 2 are indistinguishable, then swapping them should give the same state, up to a constant. That is, $\psi(q_2, q_1) = c\psi(q_1, q_2)$.
 Convince yourself that this means that $\hat{P}_{12}^2\psi(q_1, q_2) = c^2\psi(q_1, q_2)$. In conjunction with your answer to part (a), what does this tell you about the value of c ?
 - (c) Suppose $c = -1$. What happens if the two particles are at the same spatial coordinates, i.e. $q_1 = q_2$?
Hint: start with $\psi(q_1, q_1) = -\psi(q_1, q_1)$. If this is true, what can you conclude about the value of $\psi(q_1, q_1)$, and how would you interpret this result?

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2. When $c = 1$, we say that the wavefunction is *symmetric* with respect to exchange, while when $c = -1$, we say it is *antisymmetric* with respect to exchange.

With this in mind, let's consider the ground state of the helium atom, this time including spin:

- (a) One way we could incorporate spin is simply to multiply the spatial wavefunction $1s(1)1s(2)$ by spin functions $\alpha(1)$, $\beta(2)$, etc. If we do this, four possible descriptions of helium's ground state are:

1. $1s(1)\alpha(1)1s(2)\alpha(2)$
2. $1s(1)\alpha(1)1s(2)\beta(2)$
3. $1s(1)\beta(1)1s(2)\alpha(2)$
4. $1s(1)\beta(1)1s(2)\beta(2)$

In the space to the right, above, identify each of these wavefunctions as symmetric with respect to exchange of electrons 1 and 2, antisymmetric with respect to exchange, or neither.

- (b) Another way we could construct the ground state of the helium atom is using the determinant

$$\psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix}$$

Is this wavefunction symmetric or antisymmetric with respect to exchange?

Hint: you can do this by multiplying the determinant out, but there is also a more elegant way to get to the answer - what happens to the determinant of a matrix if you swap two rows or two columns?

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The Effective Potential in the Hartree Method

In this exercise, we'll think about the physical meaning of the effective potential in the Hartree Method.

1. Consider an electron with wavefunction $\phi(1) \equiv \phi(\vec{r}_1)$:
 - (a) What is the *probability density* for this electron?

 - (b) What is the probability of finding the electron in a specific volume element $d\tau_1$ near position \vec{r}_1 ?

 - (c) On average, how much charge is in this volume element $d\tau_1$? (Remember that a single electron has charge e .)

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- (d) Suppose there is another electron (let's call it electron 2) at position \vec{r}_2 . What is the potential energy for the interaction between electron 2 and the little piece of electron 1's charge in volume element $d\tau_1$ near position \vec{r}_1 ?
- (e) What is the total potential energy for electron 2 at position \vec{r}_2 interacting with electron 1 (i.e. what do we get if we integrate over all possible positions of electron 1)?
- (f) Compare your answer to part (e) with the following expression for V_{eff} , the effective potential in the Hartree method:

$$V_{eff}(\vec{r}_2) = \int d\tau_1 \phi^*(1) \frac{e^2}{4\pi\epsilon_0 r_{12}} \phi(1)$$

Explain, in your own words, why we might say that V_{eff} is the potential that electron 2 “sees” when it interacts only with the average charge distribution of electron 1.

STOP HERE.

First-Order Perturbation Theory

For a perturbed Hamiltonian, $\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}$, we can write the full solutions to the Schrödinger equation as expansions of the form

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad |n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots$$

In this set of exercises, we'll consider a simplified version of this problem where only keep terms that are zeroth and first order in λ , e.g.

$$E_n \approx E_n^{(0)} + \lambda E_n^{(1)} \quad |n\rangle \approx |n^{(0)}\rangle + \lambda |n^{(1)}\rangle$$

1. (a) Substitute the above expressions for \hat{H} , $|n\rangle$, and E_n into the Schrödinger equation ($\hat{H} |n\rangle = E_n |n\rangle$) and multiply out both sides of the resulting equation.

- (b) If $\lambda = 0$, what equation results? Discuss, in your group, why this makes physical sense.

- (c) Because the equation from part (a) must hold for *any* value of λ , the terms that scale as λ on the left side must be equal to the ones that scale as λ on the right side (the same would be true for the terms that scale as λ^2 , but we haven't included all of those, so we'll ignore them for now).

If you include only the terms that have exactly one factor of λ , what equation results?

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2. If we overlap both sides of this equation with $\langle n^{(0)}|$, we obtain

$$\underbrace{\langle n^{(0)}|H^{(1)}|n^{(0)}\rangle}_A + \underbrace{\langle n^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle}_B = \underbrace{\langle n^{(0)}|E_n^{(1)}|n^{(0)}\rangle}_C + \underbrace{\langle n^{(0)}|E_n^{(0)}|n^{(1)}\rangle}_D$$

- (a) Term C is easy to simplify, as long as we require that the zeroth-order states (the $|n^{(0)}\rangle$) are orthonormal. If this is true, what is term C equal to?
- (b) We usually also require that the first-order corrections are orthogonal to the zeroth-order states, e.g. $\langle n^{(0)}|n^{(1)}\rangle = 0$ (this requirement is called *intermediate* normalization). If this is true, how can you simplify term D ?
- (c) Term B is trickier, but if we remember that $\hat{H}^{(0)}$ is Hermitian, we can rewrite it as $\langle n^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle = \langle n^{(1)}|\hat{H}^{(0)}|n^{(0)}\rangle^*$. Using this trick, and remembering that $\hat{H}^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$, how can you simplify this term?
- (d) Substitute your answers to parts a-c in to the equation at the top of the page. In your group, discuss what the resulting equation tells you about the relationship between the zeroth-order states and the first-order corrections to the energy and Hamiltonian.

STOP HERE.

Degenerate Perturbation Theory

As discussed in class, the approach described in the previous exercise fails when any of the zeroth-order states are degenerate. In this exercise, we'll consider how to transform our basis set to solve this problem.

1. (a) Suppose the states $\{|i^{(0)}\rangle\}$ are degenerate, i.e. $\hat{H}^{(0)} |i^{(0)}\rangle = E |i^{(0)}\rangle$ for all of the states with different i . Calculate $H^{(0)} |n^{(0)}\rangle$, where $|n^{(0)}\rangle$ is a linear combination of these states, e.g. $|n^{(0)}\rangle = \sum_i c_{in} |i^{(0)}\rangle$.

-
- (b) Explain why your result means that we can change our basis to any linear combination of the degenerate eigenfunctions without changing the result of our calculation.

2. An “easy” solution to our degeneracy problem is to require that the numerator, $\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle$, equals zero whenever $n \neq m$.

(a) Substitute $|n^{(0)}\rangle = \sum_i c_{in} |i^{(0)}\rangle$ and $|m^{(0)}\rangle = \sum_j c_{jm} |j^{(0)}\rangle$ into $\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle$ and simplify the expression until it is in terms of c_{in} , c_{jm} , and $H_{ji}^{(1)}$ (where $H_{ji}^{(1)} = \langle j^{(0)} | \hat{H}^{(1)} | i^{(0)} \rangle$ are the matrix elements of the perturbation Hamiltonian).

(b) Remembering that $c_{jm}^* = (\underline{c}^\dagger)_{mj}$, how can you rewrite this expression using a matrix product?

(c) In order for $\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle$ to be nonzero when $n = m$ but zero otherwise, the resulting matrix must be a *diagonal* matrix.

Explain, in words, what this means about the matrix \underline{c} containing the coefficients c_{in} .

STOP HERE.